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PROCESS FOR TERMINATING THE ORGANOLITHIUM CATALYSIS OF DIENE POLYMERIZATION AND PRODUCT RESULTING THEREFROM

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This invention relates to reacting polymeric materials. In one aspect the invention relates to reacting a polymer terminated with an alkali metal atom. In another aspect the invention relates to polymeric materials prepared by terminating terminally reactive polymer prepared in the presence of an organoalkali metal initiator.

This is a continuation-in-part of a patent application, Ser. No. 772,167, filed Nov. 6, 1958, by Carl A. Uraneck et al., now U.S. Patent 3,135,716.

As used herein, the term "terminally reactive polymer" designates polymer which contains a reactive group at either or both ends of the polymer chain. The term "monoterminally reactive polymer" designates polymer which contains a reactive group only at one end of the polymer chain.

It has been discovered that new and useful polymers can be prepared by polymerizing polymerizable monomers to liquid, solid, or semisolid polymers which contain reactive groups at either one or both ends of the polymer chain and double bonds within the polymer chain. New and useful solid materials can also be obtained by reacting and/or curing these terminally reactive polymers.

The monomers which can be employed in the preparation of these terminally reactive polymers include a wide variety of materials. The preferred monomers are the conjugated dienes containing from 4 to 12 carbon atoms and preferably 4 to 8 carbon atoms, inclusive, per molecule. The term "polymer" as defined herein includes both homopolymers and copolymers. Examples of suitable conjugated dienes that can be polymerized to form terminally reactive polymers which can be terminated by the method of this invention are: 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene), 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene (piperylene), 2-methyl-1,3-hexadiene, 2-phenylbutadiene, 3-methyl-1,3-pentadiene, 2-phenyl-3-ethylbutadiene, 1,3-octadiene, and the like.

In addition, conjugated dienes containing reactive substituents along the chain can also be employed, such as for example, halogenated dienes, such as chloroprene, fluoroprene, etc. Of the conjugated dienes the preferred material is butadiene, with isoprene and piperylene also being especially suitable.

In addition to the conjugated dienes other monomers which can be employed, either alone or in admixture with the conjugated dienes, are compounds containing an active $CH_2=C<$ group. Inclined among these latter compounds are vinyl-substituted aromatic compounds including, but not limited thereto, styrene, paramethoxystyrene, divinylbenzene, 3,-vinyltoluene, 1-vinylnaphthalene, 2-vinylnaphthalene, 3-methylstyrene, 2-vinylanthracene, 3-vinylfluorene and the like. Preferably the viny-substituted aromatic compounds contain 8 to 16 carbon atoms per molecule, more preferably 8 to 12 carbon atoms per molecule. Other monomers in this group include heterocyclic nitrogen-containing monomers, such as pyridine and quinoline derivatives containing at least 1 vinyl or alphamethylvinyl groups, such as 2-vinylpyridine, 3-vinylpyridine, 4-vinylpyridine, 3-ethyl-5-vinylpyridine, 3-methyl - 5 - vinylpyridine, 2-methyl-5-vinylpyridine, 3,5-diethyl-4-vinylpyridine, etc.; similar mono- and di-substituted alkenyl quinolines; acrylic acid esters, such as methyl acrylate, ethyl acrylate; alkacrylic acid esters, such as methyl methacrylate, ethyl methacrylate, propyl methacrylate, ethyl ethacrylate, butyl methacrylate; nitriles such as acrylonitrile, and the like.

The term polymer as defined herein includes not only homopolymers and random copolymers of the above materials, but also block copolymers which are formed by polymerizing a monomer onto the end of a polymer, the monomer being introduced in such a manner that substantially all of the co-reacting molecules enter the polymer chain at this point. The block copolymers can include combinations of homopolymers and copolymers of the above materials hereinbefore set forth.

These terminally reactive polymers are prepared by contacting the polymerizable monomer or monomers with an organoalkali metal compound. The organoalkali metal compounds preferably contain from 1 to 4 alkali metal atoms, including lithium, sodium, potassium, rubidium and cesium, with those containing one or two alkali metal atoms being more often employed. Lithium is the preferred alkali metal.

The organoalkali metal compounds can be prepared in several ways, for example by replacing halogens in an organic halide with alkali metals, by direct addition of alkali metals to a double bond, or by reacting an organic halide with a suitable alkali metal compound. These organoalkali metal compounds are hereinafter described in more detail.

It is known that certain elastomeric hydrocarbon polymers and copolymers, particularly certain polymers of conjugated dienes, have a tendency to cold flow in the unvulcanized state. For example, in the event that cracks or punctures develop in a package of rubber, the polymer or copolymer tends to flow therefrom leading to product loss or contamination or causing the packages to stick together. Further, after fabrication of these materials into finished products such as automobile tires, there is a decided tendency to considerably greater heat build-up during uses involving working than that which occurs in products comprising natural rubber.

We have found an effective terminating agent for terminating the polymerization of these monomers which results in an improved product. These thus terminated polymers have a reduced tendency to cold flow and also have less heat build-up as well as other improvements in other physical properties of the polymer and finished rubber.

It is an object of the invention to provide an improved terminated terminally-reactive polymeric material.

It is another object of the invention to provide a polymer of conjugated diene.

It is another object of the invention to provide a method for terminating the polymerization of conjugated dienes with organoalkali metal catalysts.

It is yet another object of the invention to provide a method for terminating the polymerization of conjugated dienes.

These and other objects of the invention will be readily apparent to those skilled in the art from the accompanying disclosure and claims.